



INVESTOR IN PEOPLE

The Patent Office
Concept House

Cardiff Road RECEIVED

Newport 16 JAN 2004

South Wales

NP10 8QQWIPO

PCT

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

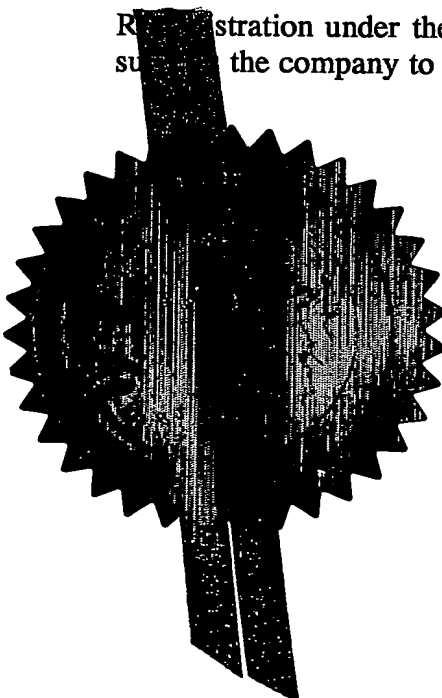
I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the application is now proceeding in the name as identified herein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Stephen Hordley

Dated 8 January 2004

BEST AVAILABLE COPY



INVESTOR IN PEOPLE

GB0314790.7

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of:-

GTL MICROSYSTEMS AG
Incorporated in Switzerland
Rigistrasse 184
CH-6340, Baar
Switzerland

ADP No. 08754038001

Patents Act 1977
(Rule)

25 JUN 2003

NEWPORT

25 JUN 03 E817722-F D02834
P01/7700 0.00-0314790.7

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference 15782 MdR

2. Patent application number
(The Patent Office will fill in this part)

0314790.7

25 JUN 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Accentus plc
329 Harwell
Didcot
Oxfordshire OX11 0QJ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

England and Wales

4. Title of the invention Catalytic reactor and process

5. Name of your agent (if you have one)

Peter Turquand MANSFIELD

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Accentus plc
Patents Dept
329 Harwell
Didcot
Oxfordshire OX11 0QJ

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country

Country

Priority application number
(if you know it)Date of filing
(day / month / year)


7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

9. Enter the number of sheets for  of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description	10
Claim(s)	2
Abstract	1
Drawing(s)	2

Handwritten: 28

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

1

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. **P.T. MANSFIELD (on behalf of Accentus plc by virtue of a Power of Attorney dated 18th February 2003)**

I/We request the grant of a patent on the basis of this application.

Signature

Handwritten signature

Date 24/6/03

12. Name and daytime telephone number of person to contact in the United Kingdom

Frances Esplin - 01235 43 2037

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

Catalytic reactor and process

This invention relates to a chemical process, and to catalytic reactors suitable for use in performing the
5 process.

A process is described in WO 01/51194 (Accentus plc) in which methane is reacted with steam, to generate carbon monoxide and hydrogen in a first catalytic
10 reactor; the resulting gas mixture is then used to perform Fischer-Tropsch synthesis in a second catalytic reactor. The overall result is to convert methane to hydrocarbons of higher molecular weight, which are usually liquid or solid under ambient conditions. The
15 two stages of the process, steam/methane reforming and Fischer-Tropsch synthesis, require different catalysts, and catalytic reactors are described for each stage. The catalytic reactors enable heat to be transferred to or from the reacting gases, respectively, as the reactions
20 are respectively endothermic and exothermic; the heat required for steam/methane reforming is provided by gas combustion. A known catalyst for the Fischer-Tropsch synthesis utilises small particles of cobalt on a ceramic support, but it has been found that this catalyst can
25 suffer oxidation or an irreversible reaction with the ceramic support in the presence of water vapour, with a resultant decrease in activity. An improved way of performing this process has now been found.

30 According to the present invention there is provided a process for performing Fischer-Tropsch synthesis using a compact catalytic reactor unit defining channels for the Fischer-Tropsch synthesis in which is a gas-permeable catalyst structure, the channels extending between
35 headers, wherein the reactor unit provides at least two successive channels for the Fischer-Tropsch synthesis

connected by a header, the gas flow velocity through the first channel being sufficiently high that no more than 65% of the carbon monoxide undergoes conversion, the gases then being cooled in the header so as to condense water vapour, and then being passed through the second channel at a sufficiently high gas flow velocity that no more than 65% of the remaining carbon monoxide undergoes conversion.

10 Preferably in both the first channel and the second channel the space velocity is above 1000 /hr, but preferably no greater than 15000 /hr. Preferably the reactor is operated so that water vapour does not exceed 20 mole%. Preferably, in each stage, no more than 60% of
15 the carbon monoxide undergoes conversion.

The space velocity, in this specification, is defined as the volume flow rate of the gases supplied to the reactor (measured at STP), divided by the void volume
20 of the reactor. Thus, if the reactor is at 210°C and a pressure of 2.5 MPa, a space velocity of 5000 /hr corresponds to a gas flow (at operating conditions) of about 354 times the void volume per hour, and so to a residence time of about 10s.

25

Thus the invention also provides a process for performing Fischer-Tropsch synthesis using a compact catalytic reactor unit defining channels for the Fischer-Tropsch synthesis in which is a gas-permeable catalyst
30 structure, wherein the synthesis is performed in at least two successive stages within the same reactor unit, at a sufficiently high flow velocity that the water vapour does not exceed 20 mole%, and that between successive stages the gases are cooled so as to condense water
35 vapour.

The invention also provides a compact catalytic reactor unit for performing such a Fischer-Tropsch synthesis, the reactor unit incorporating headers that connect successive flow channels, the headers enclosing means to condense water vapour and to remove condensed liquids from the header. The catalytic reactor unit preferably comprises a plurality of metal sheets arranged as a stack and bonded together to define channels for the Fischer-Tropsch synthesis alternating with channels for a heat exchange fluid. Preferably the temperature in the synthesis channels is above 190°C, for example 200°C. Corrugated or dimpled foils, metal meshes, or corrugated or pleated metal felt sheets may be used as the substrate of the catalyst structure within the flow channels to enhance heat transfer and catalyst surface area.

It will be appreciated that the materials of which the reactor are made are subjected to a corrosive atmosphere in use. The reactor may be made of a metal such as an aluminium-bearing ferritic steel, for example it might comprise iron with 15% chromium, 4% aluminium, and 0.3% yttrium (eg Fecralloy (TM)). When this metal is heated in air it forms an adherent oxide coating of alumina which protects the alloy against further oxidation; this oxide layer also protects the alloy against corrosion. Where this metal is used as a catalyst substrate, and is coated with a ceramic layer into which a catalyst material is incorporated, the alumina oxide layer on the metal is believed to bind with the oxide coating, so ensuring the catalytic material adheres to the metal substrate. Other stainless steels may also be used.

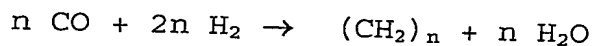
The invention will now be further and more particularly described, by way of example only, and with reference to the accompanying drawings, in which:

Figure 1 shows a sectional view of a reactor suitable for performing Fischer-Tropsch synthesis, showing a plate in plan; and

5

Figure 2 shows a modification of the reactor of figure 1.

The invention relates to Fischer-Tropsch synthesis, which may form part of a process for converting methane to longer chain hydrocarbons. Fischer-Tropsch synthesis is a reaction between carbon monoxide and hydrogen, and this gas mixture may for example be generated by steam/methane reforming. In Fischer-Tropsch synthesis the gases react to generate a longer chain hydrocarbon, that is to say:



which is an exothermic reaction, occurring at an elevated temperature, typically between 190 and 350°C, for example 210°C, and an elevated pressure typically between 2 MPa and 4 MPa, for example 2.5 MPa, in the presence of a catalyst such as iron, cobalt or fused magnetite, with a promoter. The exact nature of the organic compounds formed by the reaction depends on the temperature, the pressure, and the catalyst, as well as the ratio of carbon monoxide to hydrogen.

A preferred catalyst comprises a coating of gamma-alumina of specific surface area 140 - 450 m²/g with about 10-40% (by weight compared to the weight of alumina) of cobalt, and with a ruthenium/platinum promoter, the promoter being between 0.01% to 10% of the weight of the cobalt. There may also be a basicity promoter such as gadolinium oxide. The activity and selectivity of the

catalyst depends upon the degree of dispersion of cobalt metal upon the support, the optimum level of cobalt dispersion being typically in the range 0.1 to 0.2, so that between 10% and 20% of the cobalt metal atoms
5 present are at a surface. The larger the degree of dispersion, clearly the smaller must be the cobalt metal crystallite size, and this is typically in the range 5-15 nm. Cobalt particles of such a size provide a high level of catalytic activity, but may be oxidised in the
10 presence of water vapour, and this leads to a dramatic reduction in their catalytic activity. The extent of this oxidation depends upon the proportions of hydrogen and water vapour adjacent to the catalyst particles, and also their temperature, higher temperatures and higher
15 proportions of water vapour both increasing the extent of oxidation.

Referring now to figure 1 a reactor 10 for Fischer-Tropsch synthesis comprises a stack of Fecralloy steel
20 plates 12, each plate being generally rectangular, 450 mm long and 150 mm wide and 6 mm thick, these dimensions being given only by way of example. On the upper surface of each such plate 12 are rectangular grooves 14 of depth 5 mm separated by lands 15 (eight such grooves being
25 shown), but there are three different arrangements of the grooves 14. In the plate 12 shown in the drawing the grooves 14 extend diagonally at an angle of 45° to the longitudinal axis of the plate 12, from top left to bottom right as shown. In a second type of plate 12 the
30 grooves 14a (as indicated by broken lines) follow a mirror image pattern, extending diagonally at 45° from bottom left to top right as shown. In a third type of plate 12 the grooves 14b (as indicated by chain dotted lines) extend parallel to the longitudinal axis.

35

The plates 12 are assembled in a stack, with each of

the third type of plate 12 (with the longitudinal grooves 14b) being between a plate with diagonal grooves 14 and a plate with mirror image diagonal grooves 14a, and after assembling many plates 12 the stack is completed with a blank rectangular plate. The plates 12 are compressed together and subjected to a heat treatment to bring about diffusion bonding or they are brazed together, so they are sealed to each other. Corrugated Fecralloy alloy foils 16 (only one is shown) 50 microns thick coated with a ceramic coating impregnated with a catalyst material, of appropriate shapes and with corrugations 5 mm high, can be slid into each such diagonal groove 14 or 14a.

More preferably pairs of corrugated catalyst-coated foils 16 with corrugations about 2.4 mm high are stacked together with a flat catalyst-coated foil between them, and spot welded together, before being slid into the grooves 14 or 14a.

Header chambers 18 are welded to the stack along each side, each header 18 defining three compartments by virtue of two fins 20 that are also welded to the stack. The fins 20 are one third of the way along the length of the stack from each end, and coincide with a land 15 (or a portion of the plates with no groove) in each plate 12 with diagonal grooves 14 or 14a. Coolant headers 22 in the form of rectangular caps are welded onto the stack at each end, communicating with the longitudinal grooves 14b. In a modification (not shown), in place of each three-compartment header 18 there might instead be three adjacent header chambers, each being a rectangular cap like the headers 22. Within each of the central compartments of the headers 18 there are coolant tubes 25 that extend the entire height of the stack. At the base of each of these central compartments is an outlet duct (not shown) through which liquids condensing onto the

tubes 25 can emerge. For use, the reactor 10 is arranged with the plates 12 in substantially horizontal planes so that the coolant tubes 25 are substantially vertical.

5 In use of the reactor 10 the mixture of carbon monoxide and hydrogen is supplied to the compartments of both headers 18 at one end (the left hand end as shown) of the stack, and so gases produced by Fischer-Tropsch synthesis emerge through the compartments of both headers
10 18 at the right hand end as shown. The flow path for the mixture supplied to the top-left header compartment (as shown), for example, is through the diagonal grooves 14 into the bottom-middle header compartment, and then to flow through the diagonal grooves 14a in other plates in
15 the stack into the top-right header compartment. A coolant is supplied to the header 22 at the same end of the stack, to maintain the temperature within the reactor 10 at about 210°C, so that the coolant is at its lowest temperature at the area where heat generation is at its
20 maximum during the first stage. Hence the flows of the reacting gases and the coolant are at least partially co-current. The intention is to approach isothermal conditions throughout the reactor 10; this has the advantage of minimising the risk of any wax (i.e. very
25 long chain hydrocarbon) blocking the flow channels towards the outlet from the reaction channels if the local temperature drops below about 190°C. (If wax deposits occur, they may be removed by raising the coolant temperature by between 5° and 15°C, and feeding
30 hydrogen-rich tail gas through the reactor.) The flow rate (space velocity) of the reacting gases is in the range 1000 - 15000 /hr, so as to ensure that the conversion of carbon monoxide is only about 60% or less by the time the gases reach the middle compartments of
35 the headers 18.

The coolant tubes 25 are supplied with coolant at a different temperature so that they are cooler, for example at 150°C (which is below the boiling point of water at the pressure in the reactor). Consequently water vapour (and some of the longer-chain hydrocarbons) condense on the outer surface of the coolant tubes 25, and runs down those tubes 25 to emerge from the outlet duct (not shown) at the bottom of the stack. This significantly reduces the partial pressure of water vapour in the gas mixture that flows on into the next set of diagonal grooves 14 or 14a. The result is that the Fischer-Tropsch synthesis takes place in two successive stages - the first stage being as the gas flows from the inlet compartments of the headers 18 to the middle compartments; and the second stage being as the gas flows from the middle compartments to the outlet compartments - and at least part of the water vapour generated in the first stage is removed from the gas stream before it enters the second stage.

20

It will be appreciated that the reactor 10 may be modified in various ways, and that in particular the plates 12 may be of different thicknesses. For example the plates 12 defining the diagonal grooves 14 and 14a in which Fischer-Tropsch synthesis takes place might be 10 mm thick with grooves 9 mm deep, while the plates 12 with longitudinal grooves 14b for the coolant might be only 4 mm thick with 3 mm deep grooves. In this case the corrugated foils 16 might be replaced by a stack of say three or four corrugated foils which may be spot welded together so the overall height is 9 mm. Such deeper grooves provide an advantage if any waxy material is produced, as they are less vulnerable to blockage. Channels greater than about 2 mm deep improve the bulk transport properties of the corrugated catalyst insert 16; in the case of Fischer-Tropsch synthesis this enables

efficient drainage and removal of liquid products, and transfer of reactant gases to the surface of the catalyst. The pitch or pattern of the corrugated foils 16 may vary along a reactor channel 14 or 14a to adjust
5 catalytic activity, and hence provide for control over the temperatures or reaction rates at different points in the reactor 10. Furthermore the diagonal grooves may decrease in width, and possibly also depth, along their length, so as to vary the fluid flow conditions, and the
10 heat or mass transfer coefficients.

During the synthesis reaction the gas volume decreases, and by appropriate tapering of the channels 14 the gas velocity may be maintained as the reaction
15 proceeds, to maintain the target conversion. An alternative way of maintaining the gas velocity is to decrease the number of flow channels, as shown in figure 2, to which reference is now made. This shows a view corresponding to that of figure 1. The only difference
20 is that the diagonal grooves 14 (and 14a) defining the second stage of the Fischer-Tropsch synthesis, that is to say the grooves 14 (and 14a) between the middle compartment and the right hand compartment of the headers 18, are separated by wider lands 30, so that there are
25 only three such grooves in each plate 12.

It will also be appreciated that a modified reactor might provide more stages, for example being a three stage Fischer-Tropsch reactor, the headers 18 defining
30 four successive compartments along each side of the reactor, and with condenser tubes 25 in each of the two middle compartments. The overall conversion may be substantially the same, for example two 60% conversion stages and three 50% conversion stages would each provide
35 an overall conversion above 80%.

Removal of the water vapour and the lower boiling point hydrocarbons onto the condenser tubes 25 not only lowers the partial pressure of water vapour and so suppresses the oxidation of the catalyst, but has the further benefit of removing at least some of those hydrocarbons that would form a liquid layer on the catalyst structure. Any such a liquid layer inhibits contact of the gas mixture with the catalyst particles and inhibits diffusion of the product hydrocarbons away from the catalyst particles, so removal of the hydrocarbons liquid minimises these diffusional resistances.

In figures 1 and 2 only four condenser tubes 25 are shown in each middle compartment, but it will be appreciated that there might be a different number of tubes, for example ten or more. And to enhance heat transfer each tube 25 may be provided with fins, preferably fins extending longitudinally so that flow of condensed liquid down the tube 25 is not impeded. Not only does water vapour condense on the tubes, but any liquid droplets entrained with the gas flow tend to impact with the surface of the tubes 25 and so are disengaged from the gas flow. As an alternative to the heat exchanger tubes 25 or other heat transfer surfaces, a spray condenser system may be provided within the middle compartments of the headers 18, which might use as the coolant fluid recycled products from the Fischer-Tropsch synthesis at about 150°C. This would be particularly beneficial if there is a risk of wax deposits fouling the heat exchanger surfaces.

Claims

1. A process for performing Fischer-Tropsch synthesis using a compact catalytic reactor unit defining channels
5 for the Fischer-Tropsch synthesis in which is a gas-permeable catalyst structure, the channels extending between headers, wherein the reactor unit provides at least two successive channels for the Fischer-Tropsch synthesis connected by a header, the gas flow velocity
10 through the first channel being sufficiently high that no more than 65% of the carbon monoxide undergoes conversion, the gases then being cooled in the header so as to condense water vapour, and then being passed through the second channel at a sufficiently high gas
15 flow velocity that no more than 65% of the remaining carbon monoxide undergoes conversion.
2. A process as claimed in claim 1 wherein in both the first channel and the second channel the space velocity
20 is above 1000 /hr, but no greater than 15000 /hr.
3. A process as claimed in claim 1 or claim 2 wherein water vapour does not exceed 20 mole%.
- 25 4. A process as claimed in any one of the preceding claims wherein, in each stage, no more than 60% of the carbon monoxide undergoes conversion.
- 30 5. A process for performing Fischer-Tropsch synthesis using a compact catalytic reactor unit defining channels for the Fischer-Tropsch synthesis in which is a gas-permeable catalyst structure, wherein the synthesis is performed in at least two successive stages within the same reactor unit, at a sufficiently high flow velocity
35 that the water vapour does not exceed 20 mole%, and that between successive stages the gases are cooled so as to

condense water vapour.

6. A compact catalytic reactor unit for performing such
a Fischer-Tropsch synthesis, the reactor unit
5 incorporating headers that connect successive flow
channels, the headers enclosing means to condense water
vapour and to remove condensed liquids from the header.

7. A reactor unit as claimed in claim 6 wherein the
10 numbers of flow channels carrying flow out of the headers
is less than the number of flow channels carrying flow
into those headers.

8. A reactor unit as claimed in claim 6 wherein the
15 cross-sectional area of the flow channels carrying flow
out of the headers is less than the cross-sectional area
of the flow channels carrying flow into the headers.

9. A process for performing Fischer-Tropsch synthesis
20 substantially as hereinbefore described with reference
to, and as shown, Figure 1 or Figure 2 of the
accompanying drawings

25

15782 Mdr

P T Mansfield
Chartered Patent Agent
Agent for the Applicant

30

Abstract

Catalytic reactor and process

5 Fischer-Tropsch synthesis is performed using a
compact catalytic reactor unit (10) defining channels in
which is a gas-permeable catalyst structure (16), the
channels extending between headers (18). The synthesis
occurs in at least two stages, as the reactor unit
10 provides at least two successive channels (14, 14a) for
the Fischer-Tropsch synthesis connected by a header, the
gas flow velocity through the first channel being
sufficiently high that no more than 65% of the carbon
monoxide undergoes conversion. The gases are cooled (25)
15 in the header between the two stages, so as to condense
water vapour, and then pass through the second channel at
a sufficiently high gas flow velocity that no more than
65% of the remaining carbon monoxide undergoes
conversion. This lowers the partial pressure of water
20 vapour and so suppresses oxidation of the catalyst.

02/01/14 14:00:00

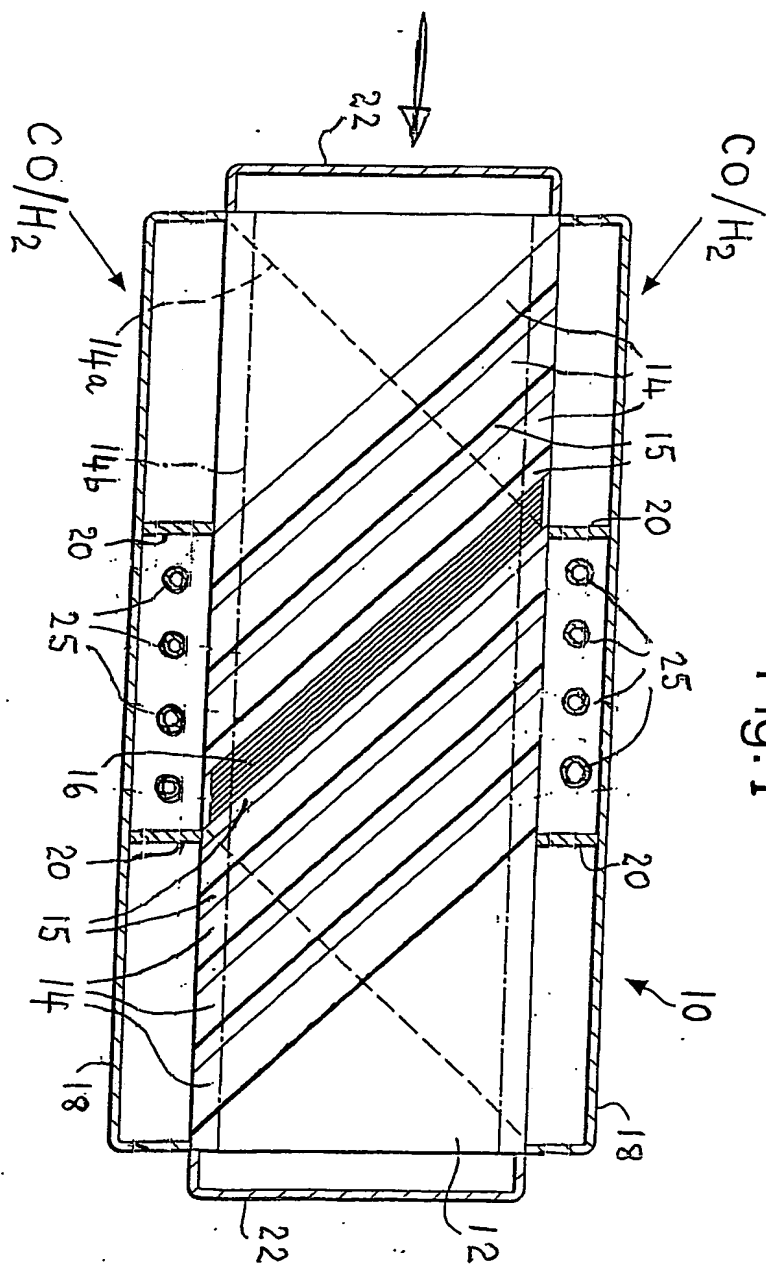


Fig. 1

P.T. Mansfield
Chartered Patent Agent
Agent for the Applicants

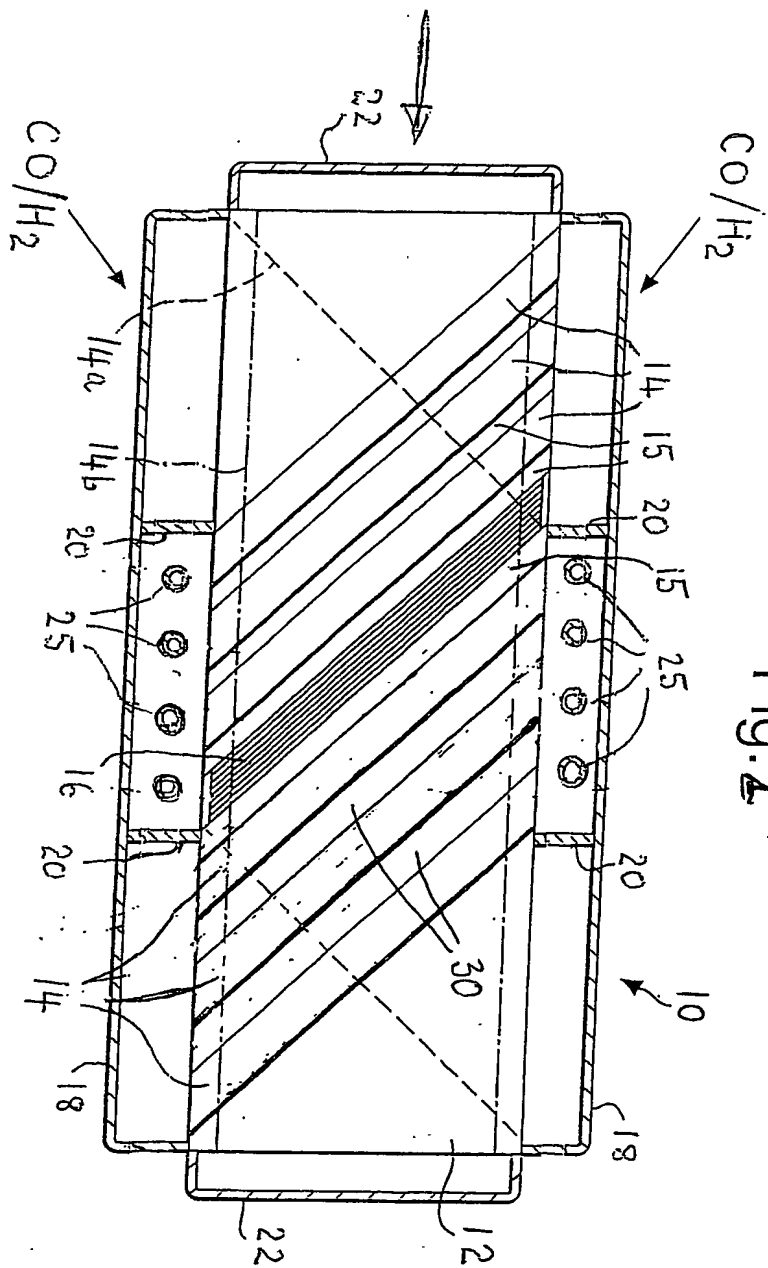


Fig. 2

P.T. Mansfield
Chartered Patent Agent
Agent for the Applicants

PCT Application

GB0305198



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.